and allowed to warm to rt. After an additional 15 h, the reaction mixture was quenched by addition of aqueous NH_4Cl and extracted with ether. Removal of the solvent left an oil which was purified by preparative TLC (hexane–ether, 3:1) to give **22b** (200 mg, 80%), **23** (8 mg, 2%), and **18** (37 mg, 15%).

22b: crystals; mp 58–59 °C; $[\alpha]^{24}_D$ -2.7° (*c* 0.83, $CHCl_3$); IR (KBr) 3080, 1740, 1720, 1640, 920, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (s, 3 H), 1.78 (s, 3 H), 1.5–3.1 (m, 8 H), 3.70 (s, 3 H), 4.65–5.10 (m, 4 H), 5.85 (dd, J = 17.3, 10.8 Hz, 1 H).

23: crystals; mp 97–98 °C; IR (film) 3070, 1740, 1730, 1640, 1210, 1165, 990, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 3 H), 1.72 (s, 3 H), 1.4–2.2 (m, 7 H), 2.50–2.66 (m, 2 H), 3.67 (s, 3 H), 3.78 (s, 3 H), 4.63–5.05 (m, 4 H), 5.80 (dd, J = 17.3, 11.0 Hz, 1 H).

13-Noreleman-8β,12-olide (25).[25] A suspension of lithium tri-*tert*-butoxyaluminium hydride (254 mg, 1.00 mmol) in THF (1 mL) was stirred and cooled to -78 °C as a solution of **22b** (63 mg, 0.25 mmol) in THF (4 mL) was added dropwise. After stirring for 30 min at -78 °C, the reaction temperature was raised to rt over 7 h. Excess hydride reagent was decomposed by addition of wet ether followed by aqueous HCl, and the product was extracted with ether. Removal of the solvent followed by filtration of an oily residue through a short silica gel column (hexane–ether, 1:1) gave **24** (59 mg, 94%) as an oil: ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.75 (s, 3 H), 1.3–2.1 (m, 7 H), 2.31–2.55 (m, 2 H), 3.68 (s, 3 H), 3.97 (br s, 1 H), 4.6–5.05 (m, 4 H), 5.75 (dd, J = 17.5, 10.5 Hz, 1 H).

A mixture of **24** (25 mg, 0.1 mmol), *p*-toluenesulfonic acid (5 mg), and CH_2Cl_2 (7 mL) was stirred at rt for 3 h, washed with brine, and dried. Concentration followed by purification of a crystalline residue by preparative TLC (hexane–ether, 1:1) gave **25** (21 mg, quantitative) as crystals: mp 79–80 °C; $[\alpha]^{25}_D$ +16.3° (*c* 0.51, $CHCl_3$); IR (KBr) 3060, 1760, 1156, 950, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.72 (s with fine splittings, 3 H), 1.4–2.9 (m, 8 H), 4.51–4.67 (m, 2 H), 4.80–4.98 (m, 2 H), 5.02 (s with fine splittings, 1 H), 5.75 (dd, J = 17.5, 10.5 Hz, 1 H).

Eleman-8β,12-olide (17).[25] The lithium enolate of **25** prepared from LDA, generated from a 1.5 M solution of BuLi in THF (0.46 mL, 0.71 mmol) and diisopropylamine (110 μ L, 0.79 mmol) in THF (6 mL), and **25** (128 mg, 0.58 mmol) was treated with phenylselenenyl chloride (126 mg, 1.03 mmol) in THF (3 mL) at -78 °C to give **26a** (147 mg, 67%), **26b** (30 mg, 14%), and recovered **25** (23 mg, 18%).

26a: oil; IR ($CHCl_3$) 3080, 1770, 1640, 1580, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 3 H), 1.68 (s, 3 H), 1.2–2.45 (m, 6 H), 3.70 (s, 1 H), 4.56 and 5.00 (s, 1 H each), 4.75 (m, 1 H), 4.8–4.9 (m, 2 H), 5.72 (dd, J = 17.5, 10.5 Hz, 1 H), 7.2–7.38 (m, 3 H), 7.48–7.55 (m, 2 H).

26b: crystals; mp 119–120 °C; IR ($CHCl_3$) 3080, 1780, 1640, 1580, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 3 H), 1.72 (s, 3 H), 1.2–2.7 (m, 6 H), 4.50 (d, J = 5.6 Hz, 1 H), 4.5 (m, 1 H), 4.62–5.01 (m, 4 H), 5.72 (dd, J = 17.0, 10.5 Hz, 1 H), 7.2–7.35 (m, 3 H), 7.5–7.75 (m, 2 H).

The lithium enolate of **26a** prepared from LDA, generated from a 1.59 M solution of BuLi in THF (1.59 mL, 0.7 mmol) and diisopropylamine (160 μL, 1.1 mmol) in THF (6 mL), and **26a** (156 mg, 0.42 mmol) were treated with MeI (71 mg, 0.50 mmol) to give **27** (97 mg, 60%) as crystals: mp 134.5–135 °C; IR ($CHCl_3$) 3080, 1765, 1620, 1580, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 3 H), 1.35 (s, 3 H), 1.68 (s, 3 H), 1.4–2.5 (m, 6 H), 4.60–5.05 (m, 5 H), 4.78 (dd, J = 17.5, 10.8 Hz, 1 H), 7.2–7.43 (m, 3 H), 7.6–7.8 (m, 2 H).

A solution of **27** (88 mg, 0.23 mmol) and pyridine (0.1 mL) in THF (3 mL) was stirred and cooled at 0 °C as 30% H_2O_2 (0.5 mL) was added, and the resulting solution was stirred at rt for 30 min. Workup gave **17** (46 mg, 88%) as an oil: $[\alpha]^{20}_D$ +100.9° (*c* 0.65, $CHCl_3$); HRMS calcd for $C_{15}H_{20}O_2$ *m/z* 232.1465, found *m/z* 232.1469. The ^1H NMR (400 MHz) spectral data of the synthetic **17** are identical with those reported for racemic **17**.[19c]

Registry No. **1**, 38651-65-9; **6**, 128261-63-2; **7**, 128301-59-7; **8**, 128261-64-3; (3*R*)-**9**, 128261-70-1;)3*S*)-**9**, 128261-65-4; **9** sulfoxide, 137041-00-0; **10**, 128261-66-5; **11**, 128261-67-6; **12a**, 1826-67-1; **12b**, 7103-09-5; **12c**, 97344-88-2; **12d**, 34164-50-6; (3*R*)-**13a**, 137041-01-1; (3*S*)-**13a**, 137041-21-5; (3*R*)-**13b**, 137041-02-2; (3*S*)-**13b**, 137041-22-6; (3*R*)-**13c**, 137041-03-3; (3*S*)-**13c**, 137041-23-7; (3*R*)-**13d**, 137041-04-4; (3*S*)-**13d**, 137041-24-8; **14a**, 128261-62-1; **14b**, 137041-05-5; **14c**, 137041-06-6; **14d**, 137041-07-7; **15a**, 128261-61-0; **15b**, 137041-08-8; **15d**, 137041-09-9; **16**, 137041-12-4; **17**, 137041-20-4; **18**, 137041-10-2; **19**, 137041-11-3; **22b**, 137041-13-5; **23**, 137041-14-6; **24**, 137041-15-7; **25**, 137041-16-8; **26a**, 137041-17-9; **26b**, 137041-18-0; **27**, 137041-19-1; (-)-β-pinone, 18172-67-3.

Supplementary Material Available: Full experimental and physical data ($[\alpha]^{20}_D$, IR, ^1H NMR) of compounds **15b,d** (2 pages). Ordering information is given on any current masthead page.

Thermal Rearrangements of α-(Acyloxy)silanes. 2. Formation of Chiral Precursors and Migratory Preference of Silicon-Based Groups

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Received May 13, 1991

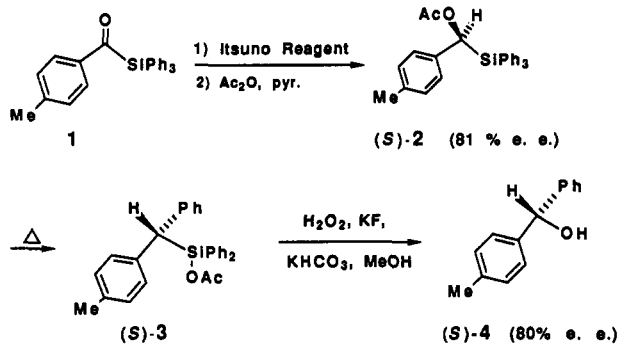
The asymmetric reduction of acylsilanes to chiral α-hydroxysilanes and the thermal rearrangement of the corresponding chiral α-acetoxysilanes was explored. Ipc_2BCl reduces many acylsilanes in >95% ee. The rate of the thermal rearrangement of the α-acetoxysilanes was dependent upon the substituents at both silicon and carbon. Evidence is presented to indicate there is electron deficiency at the α-carbon in the transition state. Migratory aptitudes follow those expected on the basis of the migrating group assuming an apical migratory group at a pentacoordinate silicon. A previously unreported hydrolytic transformation of a proposed acylsilyl hydride to a stable 1-sila-1,2-diol was observed.

Brook,[1] Reetz,[2] and Tacke[3] have demonstrated that α-acetoxysilanes (e.g., **2**) can be thermally rearranged to the corresponding silyl acetates with concurrent migration of one aryl group from silicon to carbon (as shown). Larson[4] studied the stereochemistry of a similar rearrangement of α-chlorosilanes. We recently reported a thermal rearrangement of α-acetoxysilanes which can be incorporated into synthetic methodology leading to the preparation of chiral non-silicon-containing secondary alcohols in reasonably high enantiomeric excess (Scheme

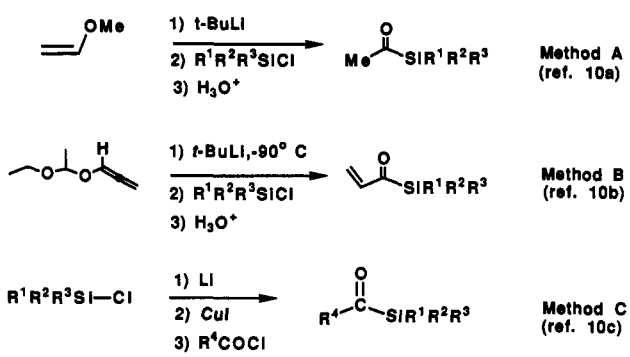
(1) (a) Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Lennon, J. M. *Can. J. Chem.* **1975**, *53*, 332. (b) Brook, A. G.; Jones, P. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1324.
(2) Reetz, M. T.; Greif, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 712.
(3) Tacke, R.; Lange, H. *Chem. Ber.* **1983**, *116*, 3685.
(4) Larson, G. L.; Klesse, R.; Cartledge, F. K. *Organometallics* **1987**, *6*, 2250.

0022-3263/91/1956-7076$02.50/0

Scheme I



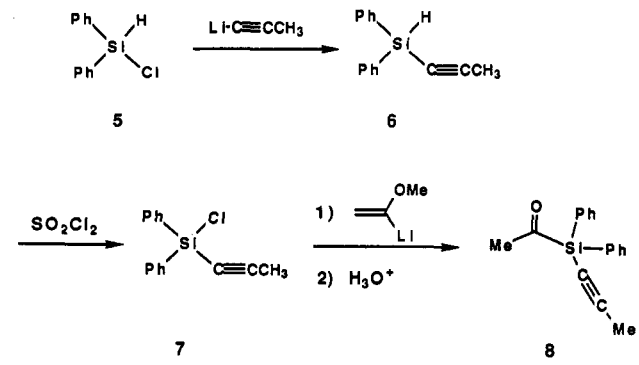
Scheme II. Methods Utilized for the Preparation of Acylsilanes



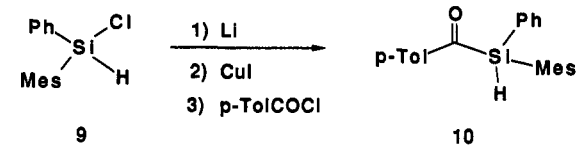
I).[5] Using a 2:1 complex of borane and (*S*)-(−)-2-amino-3-methyl-1,1-diphenylbutan-1-ol, a chiral reducing system originally discovered by Itsuno,[6] we were able to reduce three acylsilanes in 50% to 94% ee. We also showed that these chiral α-hydroxysilanes could be acylated and thermally rearranged. The resultant silafunctional compounds were subsequently oxidized[7,8] to produce secondary alcohols without the loss of chirality. The process is particularly useful in the production of chiral secondary (non-silicon-containing) carbinols with nearly identical R groups (e.g., 4) which cannot be prepared by reduction of the corresponding ketone with available chiral reducing agents.

Recently, Soderquist[9] has reported that (−)-Ipc_2BCl can function as a reducing agent of acylsilanes. We have also been exploring the reduction of acylsilanes by this reducing agent and would now like to report the results of our studies, which include the following: (1) the proficiency with which (−)-Ipc_2BCl can function as a chiral reducing agent of acyl silanes; (2) the effect of substituents on the rate of the thermal rearrangement of α-acetoxytriphenylsilanes; (3) the generation of unusually functionalized acylsilanes; and (4) the migratory proficiency of silyl alkyl groups in this thermal rearrangement. In some model cases the resultant chiral silafunctional compounds were oxidatively cleaved to the non-silicon-containing alcohols demonstrating the stereospecificity of the overall process.

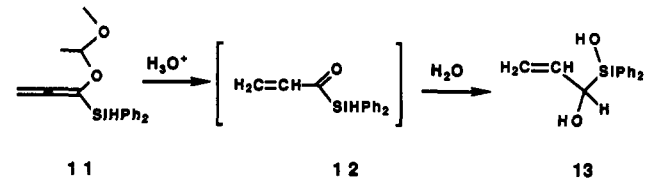
Scheme III



Scheme IV



Scheme V



Results

Preparation of Acylsilanes. As shown in Scheme II, acylsilanes were prepared by three established methods.[10] Existing procedures for the preparation of acylsilanes have certain synthetic limitations. Methods A and B allowed the preparation of acylsilanes with a diverse range of (acid-stable) groups on silicon. However, these methods produce only acetyl and propenoyl groups, respectively, on the alkyl side of the carbonyl. Method C involves the intermediacy of a silyl anion. This protocol is capable of accomodating a wider variety of substituents on the alkyl side of the carbonyl, but is limited to arylsilanes, which form silyl anions readily from the corresponding chlorosilane. The preparation of trialkylsilyl anions is significantly less convenient, usually requring HMPA as a solvent. The difficulties in the preparation of trialkylsilyl anions are discussed in a recent book.[11]

One of the objectives of the present research was to investigate the relative migratory aptitude of different silicon-based substituents. In particular, relatively small groups, such as hydrogen and alkynes, were expected to migrate rapidly due to their ability to attain an apical position on a proposed trigonal bypyrimidal silicon intermediate. Schemes III and IV illustrate the preparation of (acylsilyl)acetylenes and acylsilyl hydrides, via procedures A and C, respectively.

While we were successful in the preparation and isolation of *p*-toluoylmesitylphenylsilane (as shown above), an attempt to prepare a diphenylpropenoylsilyl hydride using method B resulted in the isolation of the unsaturated α-hydroxysilanol **13** as shown in Scheme V. The X-ray

(5) Buynak, J. D.; Strickland, J. B.; Hurd, T.; Phan, A. *J. Chem. Soc., Chem. Commun.* **1989**, *89*.
(6) Itsuno, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Ito, K. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2039.
(7) For leading references see: (a) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. (b) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090.
(8) For a leading reference see: Fleming, I.; Sanderson, P. E. G. *Tetrahedron Lett.* **1987**, *36*, 4229.
(9) Soderquist, J. A.; Anderson, C. L.; Miranda, E. I.; Rivera, I.; Kabalka, G. W. *Tetrahedron Lett.* **1990**, *31*, 4677.
(10) (a) Soderquist, J. A.; Hsu, G. J. H. *Organometallics* **1982**, *1*, 830. (b) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949. (c) Duffaut, N.; Dunogues, J.; Biran, C.; Calas, R. *J. Organomet. Chem.* **1978**, *161*, C23.
(11) *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: New York, 1988; Vol 11, pp 178–185.

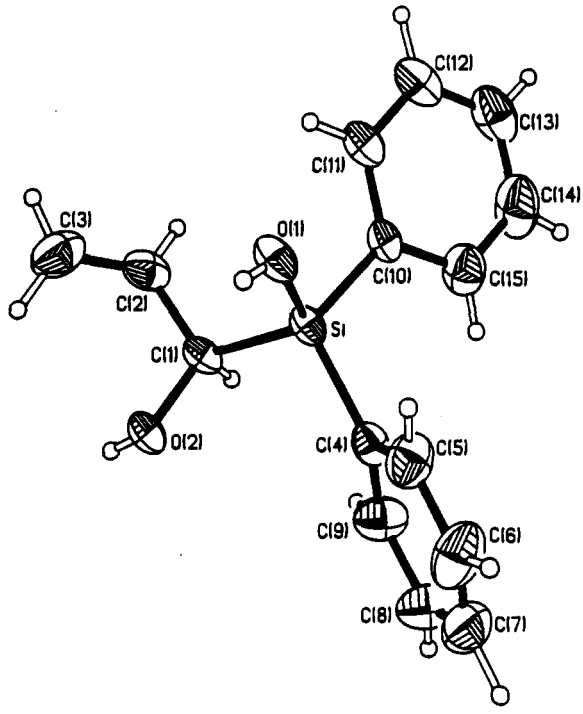


Figure 1. ORTEP drawing of compound 13.

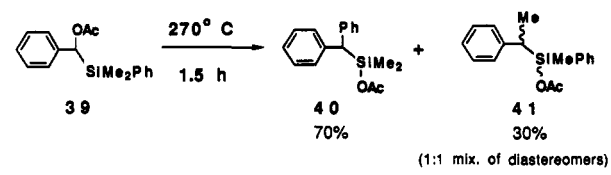
crystal structure shown in Figure 1 confirms the identity of this unusual product. Literature searching[12] reveals that this is the first example of an air- and moisture-stable 1-sila-1,2-diol. It should be noted that acetyldi-*tert*-butylsilane and acetyldi-*tert*-butylfluorosilane have been prepared using similar methodology.[13] Apparently, steric bulk at silicon is necessary to prevent reduction of the carbonyl by the silyl hydride under the acidic conditions necessary for hydrolysis of the enol ether. It is not known whether the mechanism of this hydride transfer is intramolecular or intermolecular.

The Reducing Agent. Upon investigation of the considerable literature on chiral reducing agents, the conclusion was drawn that, in addition to the Itsuno reagent[6] already explored, two other agents were worthy of consideration. These were the chlorodiisopinocampheylborane system developed by Brown[14] and the chiral binaphthol system developed by Noyori.[15] As this work progressed, a paper appeared which indicated the Noyori reagent to be a superior reagent for the reduction of acylstannanes.[16] However, in preliminary studies, we were unable to obtain satisfactory enantiomeric excess by using this reagent in the reduction of acylsilanes. We thus chose to limit our investigation to Ipc_2BCl. Our studies showed that this relatively inexpensive, commerically available reagent provides high enantiomeric excess in the reduction of most acylsilanes.

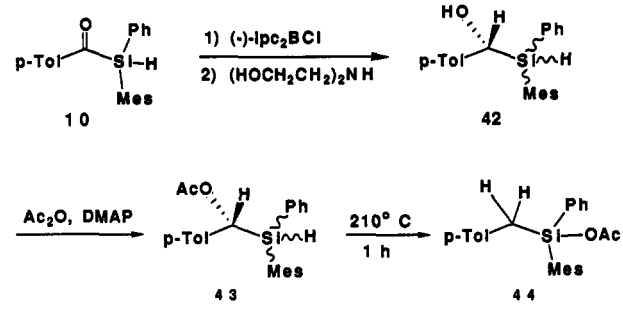
Reduction was achieved by treatment of an approximately 0.3 M solution of acylsilane in THF with 1.5 equiv of (+)- or (−)-Ipc_2BCl at room temperature overnight. The resulting boronates were cleaved by treatment with diethanolamine, and the product silylcarbinols were purified

(12) CAS Online, 1967–1990.
(13) Dexheimer, E. M.; Spialter, L. *J. Organomet. Chem.* **1976**, *107*, 229.
(14) Chandrasekharan, J.; Ramachandran, P. V.; Brown, H. C. *J. Org. Chem.* **1985**, *50*, 5446. (b) Brown, H. C.; Chandrasekharan, J.; Ramachandran, P. V. *Ibid.* **1986**, *51*, 3394.
(15) (a) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. (b) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *Ibid.* **1984**, *106*, 6717.
(16) Chan, P. C. M.; Chong, J. M. *J. Org. Chem.* **1988**, *53*, 5584.

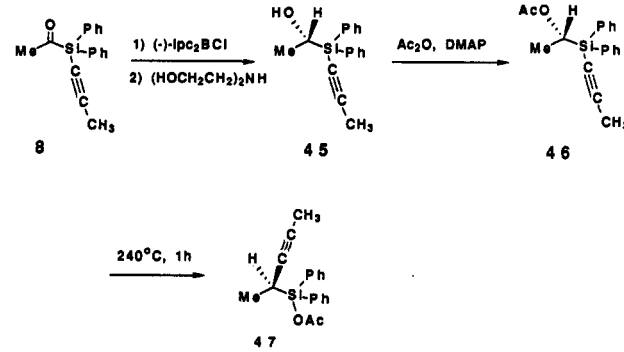
Scheme VI



Scheme VII



Scheme VIII



by column chromatography. Enantiomeric excess (ee) was measured by conversion to the Mosher ester and analysis of either ^{19}F NMR spectra or ^1H NMR spectra with or without the use of $Eu(fod)_3$ shift reagent.[17] Assignment of absolute configuration was made by analogy with Brown's results on hindered ketones and the crystal structure of a Mosher derivative of one silylcarbinol that was prepared in our laboratory. Our results agree with those recently published by Soderquist.[9]

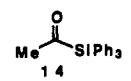
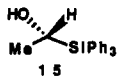
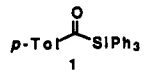
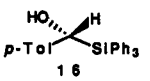
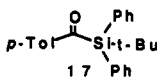
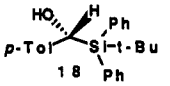
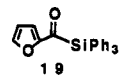
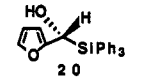
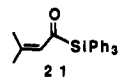
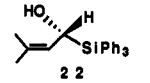
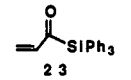
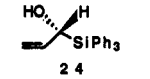
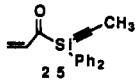
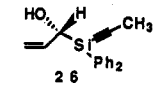
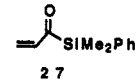
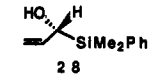
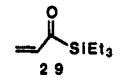
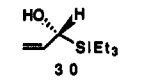
Synthesis of α-Acetoxysilanes. Except in cases where the silyl substituent was extremely bulky, acetates of these alcohols were easy to prepare. The esters were formed by simple treatment with acetic anhydride in the presence of pyridine using a catalytic amount of DMAP. To establish enantiomeric excess, Mosher esters were prepared from 1 equiv of alcohol, 2 equiv of Mosher chloride, and 4 equiv of DMAP in dry CH_2Cl_2. Typical reaction times varied from a few hours to overnight.

The Thermal Rearrangement. In the course of performing the thermolyses, it was observed that substituents at both carbon and silicon affect the rate of the overall process. Table II lists the temperatures required for complete rearrangement of a variety of α-acetoxytriphenylsilanes (stereochemistry not shown) within 1 h. In all cases, thermolysis was performed on the neat α-acetoxysilane in an evacuated sealed tube.

The relative rates of rearrangement of the compounds with aryl side chains suggest that electron-donating groups at carbon lower the activation energy, while electron-withdrawing groups raise it, thus indicating an electron

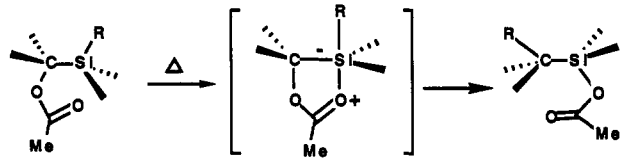
(17) Yasuhara, F.; Yamaguchi, S. *Tetrahedron Lett.* **1977**, 4085.

Table I. Summary of Asymmetric Reductions Using (-)-Ipc$_2$BCl[a]

acylsilane	preparation	product	ee
 14	A	 15	95%
 1	C	 16	96%
 17	C	 18	95%
 19	C	 20	95%
 21	C	 22	97%
 23	B	 24	97%
 25	B	 26	89%
 27	B	 28	83%
 29	B	 30	80%

[a] A, B, and C refer to the procedure used to prepare the acylsilane. Enantiomeric excess was determined by conversion of the alcohol to Mosher esters followed by integration of the ^{19}F NMR peaks of the diastereomers.

Scheme IX



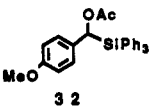
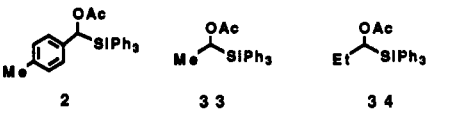
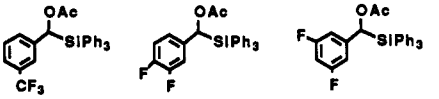
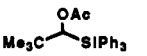
48 49 50

deficiency at the α-carbon in the transition state. It should also be noted, however, that the very slow migration of phenyl to the α-carbon of the *tert*-butyltriphenylsilylcarbinol indicates that there is also a steric component to the activation barrier.

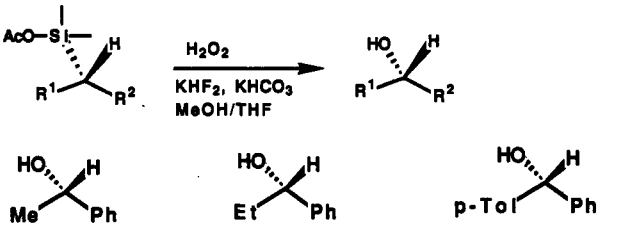
Our initial studies were conducted with triphenylsilanes, since these were easy to prepare (via the triphenylsilyl anion) and could be reduced with high enantioselectivity. To expand the synthetic utility, we explored the migratory aptitude of other groups as well. In cases where both methyl and aryl groups were present phenyl migrated faster, but not exclusively. As shown below, both acetylene and hydride could migrate rapidly and in preference to phenyl groups. The latter rearrangements occurred at slightly lower temperatures.

The approximate order of migratory aptitude was found to be H, C≡C ≫ Ph > Me. This coincides with the apicophilicity of these groups and suggests a transition state as that shown in Scheme IX. This mechanism is also

Table II. Reaction Temperature Necessary for Complete Rearrangement in 1 h for Several α-Acetoxy(triphenylsilanes)

reaction temp (°C)	thermolyzed α-acetoxytriphenylsilanes
190	 (Fastest) 31
220	 32
255	 2 33 34
265	 35 36 37
290	 (Slowest) 38

Scheme X. General Procedure for Oxidative Cleavage



97% e. e. 98% e. e. 97% e. e.

supported by the observed stereochemistry of the thermolysis reaction. Our earlier experiments showed that the configuration was inverted at carbon, and Larson's results[4] with α-chlorosilanes would suggest that inversion may also occur at silicon.

Conversion of the Silafunctional Compound to Alcohols. The conversion of the resultant silylacetates to alcohols involved treatment of the silafunctional compound with an oxidizing agent (H_2O_2 or *m*-CPBA), a source of fluoride (such as KF or KHF_2), and a buffer (such as $KHCO_3$) in a polar solvent (MeOH/THF or DMF). The reactions were monitored by thin-layer chromatography and usually occurred at room temperature or with modest heating during periods of a few hours to overnight. In this way, three chiral silafunctional compounds were converted to chiral secondary alcohols by this method. Yields for this final step ranged from 50 to 60%. The enantiomeric excess was again measured by conversion of the alcohol to a Mosher ester. Note that the measured enantiomeric excess corresponds closely (±1%) with that measured for the corresponding silyl carbinols. This result confirms the stereospecificity of the overall transformation.

Conclusion

Many acylsilanes can be reduced in high enantiomeric excess using commercially available (-)-Ipc$_2$BCl. The re-

sultant silylcarbinols can be transformed to the corresponding acetates and thermally rearranged at temperatures between 200 and 270 °C. The arylsilanes studied rearrange cleanly and in high yield. There is only partial selectivity in favor of a migrating aryl group compared with a migrating alkyl group. However, both hydride and acetylide groups migrate in complete preference to aryl groups. In cases of similar steric hindrance, electron-donating groups on carbon allow the rearrangement to proceed at lower temperatures.

Except in cases where no other methodology is available, this reaction has not yet reached a point where it is a practical and general synthetic alternative to the direct use of chiral reducing agents on non-silicon-containing ketones. This is due primarily to limitations in synthetic routes to acylsilanes and to a lack of selectivity in the migrations of groups from silicon to carbon. Studies directed toward overcoming these difficulties are currently in progress.

Experimental Section

General. Melting points were taken in glass capillary tubes using a calibrated thermometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP200SY spectrometer. Mass spectral data were obtained by either EI or FAB techniques. TLC was performed on Merck 0.2-mm Kieselgel 60 F254 silica-coated plastic plates. The compounds were identified in one or more of the following manners: UV (254 nm), I_2 chamber, and phosphomolybdic acid spray reagent. Flash chromatography was performed by using flash chromatographic techniques in thick-walled glass columns and Merck 0.040–0.063-mm Kieselgel 60 silica gel. The glassware used in the reactions described below was oven or flame dried, and then it was cooled under Ar.

The chromatography solvents were distilled from CaH_2 before use. All additional solvents were obtained from Aldrich in Sure-Seal bottles. Anhydrous reagents were used as received from Aldrich unless otherwise noted.

The enantiomeric excess of the alcohols was obtained by forming their corresponding Mosher esters (see general procedure below) and integrating the ^{19}F NMR signals of the respective diastereomers.

Optical rotations were measured using a JASCO Model DIP-360 digital polarimeter. The samples were run at ambient temperature in $CHCl_3$ as solvent using a sodium lamp (598 nm) as a light source.

Diphenylprop-1-ynylchlorosilane (7). *n*-BuLi (2.5 M in hexanes, 160 mL, 400 mmol) was added dropwise to a solution of propyne (43 mL, 759 mmol) in anhydrous THF (400 mL) while stirring at −78 °C. The cooling bath was removed, and the slurry was allowed to warm to rt over 45 min. This slurry was recooled to −78 °C and transferred by cannula to a solution of diphenylchlorosilane (83 g, 379 mmol) in anhydrous THF (400 mL) which was also at −78 °C. The reaction was allowed to stir at −78 °C for an additional 10 min then at rt for 3.5 h. Most of the THF was removed in vacuo, and the residue was dissolved in pentane (500 mL). This pentane solution was washed with water (3 × 100 mL), saturated NH_4Cl (1 × 100 mL), and brine (1 × 100 mL). After the solution was dried over Na_2SO_4, the pentane was removed in vacuo and the residue further purified by vacuum distillation to produce **diphenyl-1-propynylsilane (6)** (bp = 122–130 °C (0.3 Torr), yield = 72%): ^1H NMR ($CDCl_3$) δ 2.00 (3 H, d, J = 1 Hz), 5.12 (1 H, q, J = 1 Hz), 7.39–7.45 (6 H, m), 7.60–7.70 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 5.3, 108.3, 128.2, 130.1, 132.8, 134.4, 135.2; IR (neat) 2970, 2925, 2200, 2150, 1430, 1120, 1030, 810, 740, 700 cm^{-1}.

A solution of **6** (60.5 g, 272 mmol) in anhydrous CH_2Cl_2 (600 mL) was treated with SO_2Cl_2 (28.4 mL, 47.7 g, 354 mmol) at 0 °C. The reaction was allowed to warm to rt as the colorless mixture stirred overnight. During this time, gas was evolved. The reaction was concentrated in vacuo to yield 72 g (**7**) as a clear, colorless oil which was used without further purification. Quantitative yield. Clear colorless liquid: ^1H NMR ($CDCl_3$) δ 2.00 (3 H, s), 7.40 (6 H, m), 7.75 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 5.2, 109.2, 127.6, 128.1, 130.9, 132.8, 134.3; IR (neat) 2202 (vs), 1433 (s), 1127 (vs) cm^{-1}; HRMS calcd for $C_{15}H_{13}{}^{35}ClSi$ 256.0472, found 256.0483; LRMS 258 (39), 256 (92), 243 (28), 241 (63), 238 (12), 215 (13).

Procedures for the Preparation of Acylsilanes. Procedure A.[10a] *t*-BuLi (66 mL, 1.7 M in pentane, 112 mmol) was added to a cold (−78 °C) solution of methyl vinyl ether (10.4 mL, 6.5 g, 112 mmol) in anhydrous THF (50 mL) at such a rate so as to maintain an internal temperature of less than −60 °C. The resulting yellow suspension was allowed to slowly warm to 0 °C producing a clear, colorless solution. This solution was then recooled to −78 °C, and the chlorosilane (74 mmol) was added dropwise (or as a THF solution in the case of solid chlorosilanes) over 15 min. The reaction was allowed to warm to rt overnight. The mixture was then poured into saturated aqueous NH_4Cl and extracted with ether/pentane (1:1, 2 × 100 mL). The combined organic solutions were washed with water (2 × 100 mL) and brine (1 × 100 mL) and dried (Na_2SO_4). The solution was concentrated in vacuo (at 0 °C in the case of the more volatile enol ethers) and subjected directly to acidic hydrolysis as described below.

The crude enol ether from above was dissolved in acetone (40 mL), chilled to 0 °C, and treated with 1 N HCl (10 mL). The solution was stirred at 0 °C for an additional 15 min then at rt for 1.5 h. The reaction was then poured into water (200 mL) and extracted with ether/pentane (2 × 200 mL (1:1)). The combined organic solutions were washed with water (2 × 100 mL) and brine (1 × 100 mL) and dried over Na_2SO_4. After careful concentration in vacuo, the crude acylsilane was purified by flash chromatography on silica gel (5% ether/pentane).

Acetyldiphenylprop-1-ynoylsilane (8): yellow oil (63% yield); ^1H NMR ($CDCl_3$) δ 2.07 (3 H, s), 2.45 (3 H, s), 7.40–7.60 (6 H, m), 7.70–7.80 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 5.3 (q), 36.8 (q), 76.4 (s), 109.5 (s), 128.2, 130.5, 135.2, 240.0 (s); IR ($CDCl_3$) 2195 (vs), 1645 (m), 1430 (m) cm^{-1}.

Acetyltriphenylsilane (14): yellow solid, mp 122–123 °C; 47% yield; ^1H NMR ($CDCl_3$) δ 2.45 (3 H, s), 7.40–7.60 (9 H, m), 7.70–7.80 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 38.0, 128.2, 130.3, 131.1, 136.1; IR ($CDCl_3$) 1572, 1430, 1115 cm^{-1}; HRMS calcd for $C_{20}H_{18}OSi$ 302.1122, found 302.1123; LRMS 302 (1), 287 (5), 260 (14), 259 (100), 180 (5), 155 (3), 129 (2), 105 (6), 79 (3), 53 (3).

Procedure B.[10b] A solution of 1-(1′-ethoxyethoxy)-1,2-propadiene[18] (2.6 g, 20.3 mmol) and 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (0.07 g, 0.2 mmol, radical inhibitor) in anhydrous THF (20 mL) was chilled to −95 °C and treated with *n*-BuLi (2.5 M in hexanes, 8.4 mL, 21.0 mmol). One min after the addition was complete, the resulting light yellow solution was treated with the silyl chloride (20.3 mmol) while maintaining the internal temperature below −90 °C (a THF solution of silyl chloride was used in cases where the silyl chloride was a solid). After being stirred for 20 min at this temperature, the reaction was allowed to warm to rt over a 1-h period. The reaction was then poured into saturated NH_4Cl and extracted with ether (2 × 50 mL). The combined organic layers were washed with water (2 × 50 mL) and brine (1 × 50 mL) and dried over Na_2SO_4. The solution was concentrated in vacuo, and the crude silylated allenyl ether was hydrolyzed directly to the acylsilane as described below.

The crude allene was dissolved in acetone (20 mL) and treated with 2 N HCl (5 mL) at rt. After being stirred in the dark for 30 min, the reaction mixture was poured into water (100 mL) and extracted with ether (2 × 50 mL). The combined organic layers were then washed with water (2 × 50 mL) and brine (1 × 50 mL) and dried over Na_2SO_4. The ethereal solution was carefully concentrated in vacuo and purified by flash chromatography on silica gel (10% ether/pentane).

(±)-Diphenyl(1-hydroxyprop-2-enyl)silanol (13). The general method B above was followed in an attempt to prepare propenoyldiphenylsilane. The crude silylated allenyl ether **11** had the following ^1H NMR: ($CDCl_3$) δ 1.15 (3 H, t, J = 6 Hz), 1.45 (3 H, d, J = 4 Hz), 3.35–3.70 (2 H, m), 4.97 (1 H, s), 5.05 (1 H, q, J = 4 Hz), 5.15 (1 H, s), 5.17 (1 H, s), 7.30–7.80 (10 H, m). After hydrolysis, the dried ethereal solution was concentrated, and a white solid (**13**) remained. This solid was recrystallized from ether/hexane to yield white crystals: 41% yield; mp 98–99 °C; ^1H NMR ($CDCl_3$) δ 4.40–4.60 (2 H, m), 5.00–5.20 (4 H, m), 5.95–6.15 (2 H, m), 7.20–7.50 (12 H, m), 7.60–7.80 (8 H, m); ^{13}C

(18) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916.

NMR ($CDCl_3$) δ 67.5 (d), 110.9 (t), 127.4 (d), 129.7 (d), 133.8 (s), 134.5 (d), 137.9 (d); IR (Nujol mull) 3284–3219 (bs), 1634 (w), 1588 (w), 1428 (s), 1120 (s) cm^{-1}. Structure further confirmed by X-ray crystallography.

Propenoyltriphenylsilane (23): yellow solid, mp 80–83 °C (67% yield); R_f = 0.52 (1:9 Et_2O/hexane); ^1H NMR ($CDCl_3$) δ 5.79 (1 H, d, J = 10.7 Hz), 5.99 (1 H, d, J = 17.8 Hz), 6.65 (1 H, dd, J = 10.7 and 17.8 Hz), 7.40–7.52 (9 H, m), 7.60–7.65 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 128.1 (d), 128.7 (t), 130.1 (d), 131.5 (s), 136.1 (d), 141.3 (d), 231.7 (s); IR (CCl_4) 1605, 1485 cm^{-1}; HRMS calcd for $C_{21}H_{18}OSi$ 314.1122, found 314.1117; LRMS 314 (12), 259 (100), 181 (17), 105 (13), 57 (12).

Diphenylpropenoylprop-1-ynylsilane (25): yellow oil (29% yield); R_f = 0.29 (1:9 Et_2O/hexane); ^1H NMR ($CDCl_3$) δ 2.12 (3 H, s), 6.01 (1 H, m), 6.61 (2 H, m), 7.46 (6 H, m), 7.72 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 5.0 (q), 77.2 (s), 110.0 (s), 129.9 (d), 130.7 (t), 130.9 (d), 134.2 (s), 135.0 (d), 141.0 (d), 229.4 (s); IR (neat) 2182 (s), 1606 (m), 1579 (m) cm^{-1}; LRMS 276 (12), 221 (100), 181 (5), 105 (13), 69 (110); HRMS calcd for $C_{18}H_{16}OSi$ 276.0966, found 276.0965.

Dimethylphenylpropenoylsilane (27): yellow liquid (35% yield); R_f = 0.56 (1:9 Et_2O/hexane). Despite repeated chromatography, approximately 2% impurities remained in this material: ^1H NMR ($CDCl_3$) δ 0.56 (6 H, s), 5.89 (1 H, dd, J = 10.7, 1.0 Hz), 6.02 (1 H, dd, J = 17.9, 1.0 Hz), 6.45 (1 H, dd, J = 17.9, 10.7 Hz), 7.43 (3 H, m), 7.59 (2 H, m); ^{13}C NMR ($CDCl_3$) δ −3.9 (q), 128.1 (d), 128.9 (d), 129.7 (t), 133.8 (d), 135.0 (s), 141.0 (d), 235.2 (s); IR (neat) 1601 (s), 1461 (w) cm^{-1}; HRMS calcd for $C_{11}H_{15}OSi$ 191.0892, found 191.0892.

Propenoyltriethylsilane (29): yellow oil (50% yield); R_f = 0.48 (1:9 Et_2O/hexane); ^1H NMR ($CDCl_3$) δ 0.65–0.80 (6 H, q, J = 7 Hz), 0.80–1.00 (9 H, t, J = 7 Hz), 5.88 (1 H, dd, J = 10.0 and 1.0 Hz), 6.09 (1 H, dd, J = 17.0 and 1.0 Hz), 6.49 (1 H, dd, J = 17.0 and 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 237.2 (s), 141.9 (d), 126.7 (t), 6.9 (q), 2.7 (t); IR ($CDCl_3$) 1598, 1462 cm^{-1}; HRMS calcd for $C_9H_{18}OSi$ 170.1122, found 170.1128; LRMS 170 (8), 142 (27), 141 (13), 115 (52), 114 (18), 113 (44), 88 (15), 87 (97), 59 (100), 58 (13), 57 (27).

Procedure C.[10c] A solution of silyl chloride (40.0 mmol) and lithium shot (0.83 g, 120 mmol) in anhydrous THF (100 mL) was stirred for the appropriate time (Ph_3SiCl, 12 h, rt; t-$BuPh_2SiCl$, 3.5 h, rt). This dark green slurry was then chilled to 0 °C and transferred by cannula (leaving behind most excess Li) to a chilled (0 °C) slurry of CuI (7.6 g, 40 mmol) in anhydrous THF (10 mL). The mixture was stirred at 0 °C for 10 min, and then the acyl halide (40 mmol) was added dropwise over a 2-min period. The reaction was allowed to warm to rt overnight, and the THF was removed in vacuo at room temperature. The resulting black solid was stirred with ether (250 mL) to create a well-dispersed slurry, and the mixture was suction filtered through a 1-in. pad of silica gel. The silica gel was washed with additional ether (1 × 150 mL). The ethereal solution was treated with 3-(dimethylamino)-propylamine (30 mmol). The yellow solution was washed successively with 2 N HCl (2 × 100 mL), saturated $NaHCO_3$ (1 × 100 mL), and brine (1 × 100 mL). After being dried over Na_2SO_4, the solution was concentrated in vacuo and the acylsilane was purified by flash chromatography on silica gel (5% ether/pentane).

***p*-Toluoyltriphenylsilane (1)**: yellow solid, mp 96–98 °C (50% yield); ^1H NMR ($CDCl_3$) δ 2.38 (3 H, s), 7.18 (2 H, d, J = 7.6 Hz), 7.35–7.50 (9 H, m), 7.60–7.70 (6 H, m), 7.76 (2 H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 229.5, 143.8, 140.2, 136.3, 132.5, 130.1, 129.1, 128.8, 128.1, 21.6; IR ($CDCl_3$) 1588 (vs), 1432 (s), 1109 (s) cm^{-1}; HMRS calcd for $C_{26}H_{22}OSi$ 378.1434, found 378.1438; LRMS 378 (2), 373 (19), 217 (18), 287 (20), 259 (68), 212 (13), 181 (22), 136 (58), 119 (56), 91 (100), 65 (31).

Mesitylphenyl-*p*-toluoylsilane (10): Mesitylphenylchlorosilane (9) was prepared first from trichlorosilane as follows. To a solution of $HSiCl_3$ (40.5 g, 0.3 mol) in dry THF (200 mL) was added mesitylmagnesium bromide (300 mL, 1.0 M in THF, 0.3 mol) over a 45-min period while cooling to −78 °C. The reaction was then warmed to rt and stirred for an additional 2 h. The reaction was again cooled to −78 °C, and phenylmagnesium bromide (100 mL, 3.0 M in Et_2O, 0.3 mol) was added over a 45-min period. The reaction was then allowed to warm to rt and stirred overnight. The solvent was removed in vacuo and replaced with anhydrous pentane (500 mL). The resultant slurry was vacuum filtered to remove precipitated magnesium salts, the solvent removed, and the resultant oil distilled at reduced pressure: yield 80%; bp 137–143 °C (0.7 mm); ^1H NMR ($CDCl_3$) δ 2.47 (3 H, s), 2.61 (6 H, s), 6.30 (1 H, s), 7.05 (2 H, s), 7.54–7.85 (5 H, m).

Compound **10** was prepared from **9** as explained above in procedure C with the following differences. Lithium shot (1.4 g, 200 mmol) was added to a solution of **9** (5.2 g, 20 mmol) in anhydrous THF (200 mL) while cooling to 0 °C. The solution was allowed to stir at 0 °C for 2 h and then transferred by cannula to a slurry of the CuI (4.0 g, 21 mmol) in THF (20 mL). The remainder of the procedure was followed as usual. The product could be purified by flash chromatography (10% ET_2O/hex) as viscous yellow oil. Despite repeated chromatography, this material still contained approximately 5% unidentified impurities by ^1H NMR (yield 48%): ^1H NMR ($CDCl_3$) δ 2.29 (3 H, s), 2.34 (9 H, s), 5.78 (1 H, s), 6.88 (2 H, s), 7.30–7.80 (9 H, m); ^{13}C NMR ($CDCl_3$) δ 21.4, 21.8, 24.4, 127.8, 128.2, 128.7, 129.1, 129.6, 130.2, 130.7, 136.1, 140.0, 140.8, 144.2, 145.2, 229.2; IR (neat) 2150 (m), 1595 (s) cm^{-1}.

***p*-Toluoyldiphenyl-*tert*-butylsilane (17)**: yellow solid, mp 93–94 °C; 84% yield; ^1H NMR ($CDCl_3$) δ 1.28 (9 H, s), 2.32 (3 H, s), 7.07 (2 H, d, J = 8.2 Hz), 7.40–7.55 (6 H, m), 7.71 (2 H, d, J = 8.2 Hz), 7.80–7.90 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 19.1, 21.6, 27.5, 128.1, 128.6, 128.9, 129.8, 133.1, 136.3, 140.0, 143.4, 231.6; IR (CCl_4) 1616 (m), 1593 (vs), 1573 (m), 1428 (m), 1174 (s), 1107 (s) cm^{-1}; HRMS calcd for $C_{24}H_{26}OSi$ 358.1754, found 358.1734; LRMS 357 (8), 343 (17), 302 (33), 301 (85), 287 (34), 135 (100).

2-Furoyltriphenylsilane (19): yellow solid, mp 98–100 °C; 37% yield; ^1H NMR ($CDCl_3$) δ 6.38 (1 H, dd, J = 3.6 and 1.7 Hz), 6.65 (1 H, dd, J = 3.6 and 0.7 Hz), 7.40–7.55 (10 H, m), 7.65–7.70 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 111.9, 119.6, 128.0, 130.2, 131.5, 136.3, 146.2, 158.0, 214.7; IR ($CDCl_3$) 1592 (s), 1424 (s), 1110 (vs) cm^{-1}; HRMS calcd for $C_{23}H_{18}O_2Si$ 361.1236, found 361.1237.

(3-Methylbut-2-enoyl)triphenylsilane (21): slightly yellow solid; mp 110–112 °C; 46% yield; ^1H NMR ($CDCl_3$) δ 1.85 (3 H, bs), 2.20 (3 H, bs), 6.71 (1 H, bs), 7.40–7.55 (9 H, m), 7.60–7.70 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 21.4, 27.5, 128.1, 128.7, 130.0, 132.1, 136.2, 151.9, 231.2; IR ($CDCl_3$) 1627 (s), 1562 (s), 1425 (s), 1110 (vs) cm^{-1}; HRMS calcd for $C_{23}H_{21}OSi$ 341.1356, found 341.1364; LRMS 328 (6), 327 (21), 281 (11), 276 (8), 259 (100).

General Procedure for the Reduction of the Acylsilanes. To a solution of (+)- or (−)-Ipc_2BCl (4.0 g, 12.4 mmol) in anhydrous THF (25 mL) was added a solution of acylsilane (8.2 mmol) in THF (5 mL) dropwise while stirring at rt. The reaction mixture was then stirred at rt overnight. After the THF was removed in vacuo, the residue was dissolved in anhydrous ether (50 mL) and treated with diethanolamine (2.7 g, 26.0 mmol). This solution was then stirred for at least 2.5 h at rt, during which time a white precipitate appeared. The precipitate was separated by suction filtration, washed with an additional 50 mL of anhydrous ether, and discarded. The combined ethereal filtrate was then washed with 1 N HCl (2 × 50 mL), saturated aqueous $NaHCO_3$ (1 × 100 mL), and brine (1 × 50 mL) and dried (Na_2SO_4). Concentration in vacuo produced crude silylcarbinol which was then purified by flash chromatography on silica gel (15% ether/pentane).

(*R*)-1-(Triphenylsilyl)ethanol (15): white solid; mp 77–79 °C; 56% yield; ^1H NMR ($CDCl_3$) δ 0.99 (1 H, bs), 1.46 (3 H, d, J = 7.6 Hz), 4.23 (1 H, bq, J = 7.6 Hz), 7.25–7.40 (9 H, m), 7.50–7.65 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 20.1, 60.2, 128.0, 129.7, 133.0, 136.1; IR (CCl_4) 3592 (m), 1428 (m), 1111 (vs) cm^{-1}; HRMS calcd for $C_{20}H_{20}OSi$ 304.1278, found 304.1272; LRMS 216 (6), 260 (24), 259 (100), 200 (6), 199 (34), 181 (15), 180 (5), 105 (11), 72 (5).

(*R*)-(Triphenylsilyl)(4′-methylphenyl)methanol (16): wax (63% yield). R_f = 0.26 in 1:9 Et_2O/hexane; $[\alpha]_{589}$ = 42.3°; ^1H NMR ($CDCl_3$) δ 2.10 (1 H, bs), 2.42 (3 H, s), 5.42 (1 H, s), 7.01, 7.02, 7.05, 7.08 (4 H, AB q), 7.30–7.50 (9 H, m), 7.50–7.60 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 21.0, 69.1, 126.7, 127.7, 128.6, 129.7, 132.6, 135.9, 136.6, 139.3; IR (CCl_4) 3535 (s), 1428 (m), 1110 (s); HRMS calcd for $C_{26}H_{24}OSi$ 387.1757, found 387.1763.

(*R*)-(*tert*-Butyldiphenylsilyl)(4′-methylphenyl)methanol (18): viscous oil; 41% yield; ^1H NMR ($CDCl_3$) δ 1.22 (9 H, s), 1.92 (1 H, bs), 2.35 (3 H, s), 5.32 (1 H, bs), 6.94 (2 H, B of ABq, J = 9.4 Hz), 7.02 (2 H, A of ABq, J = 9.4 Hz), 7.48 (6 H, m), 7.74 (2 H, d, J = 6.4 Hz), 7.82 (2 H, d, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$) δ 18.9, 21.1, 18.4, 68.7, 126.9, 127.4, 128.6, 129.3, 133.2, 133.3, 135.7, 137.0, 140.5; IR (CCl_4) 3578 (m), 2859 (s), 1427 (s), 1107 (vs) cm^{-1};

HRMS calcd for $C_{24}H_{28}OSi$, 360.1902, found 360.1900; LRMS 360 (1), 239 (11), 197 (24), 181 (6), 135 (100).

(*R*)-(Triphenylsilyl)(2′-furanyl)methanol (20): viscous oil; 59% yield; R_f = 0.19 in 1:9 Et_2O/hexane; ^1H NMR ($CDCl_3$) δ 1.96 (1 H, bs), 5.38 (1 H, s), 6.07 (1 H, dd, J = 0.43, 3.6 Hz), 6.30 (1 H, dd, J = 1.8, 0.43 Hz), 7.48 (10 H, m), 7.68 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 61.3, 107.9, 110.5, 127.8, 129.8, 132.5, 136.1, 141.6, 155.4; IR ($CDCl_3$) 3565 (m), 1412 (s), 1112 (vs) cm^{-1}.

(*R*)-1-(Triphenylsilyl)-3-methylbut-2-en-1-ol (22): clear colorless oil (66% yield); R_f = 0.21 in 1:9 Et_2O/hexane; $[\alpha]_{589}$ = 64.5°; ^1H NMR ($CDCl_3$) δ 1.44 (3 H, s), 1.55 (1 H, bs), 1.75 (3 H, s), 5.07 (1 H, d, J = 10.6 Hz), 5.58 (1 H, d, J = 10.6 Hz), 7.42 (3 H, m), 7.68 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 18.1 (q), 25.8 (q), 62.9 (d), 124.8 (d), 127.7 (d), 129.6 (d), 133.1 (s), 134.1 (s), 136.2 (d); IR (neat) 3444 (bs), 1658 (w), 1429 (m), 1109 (s) cm^{-1}; HRMS calcd for $C_{23}H_{24}OSiLi$ 351.1757, found 351.1760.

(*R*)-1-(Triphenylsilyl)prop-2-enol (24): white solid (11% yield); R_f = 0.14 (1:9 Et_2O/hexane); mp 79 °C; ^1H NMR ($CDCl_3$) δ 1.75 (1 H, bs), 5.00 (1 H, m), 5.20 (2 H, m), 6.26 (1 H, m), 7.43 (9 H, m), 7.82 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 67.6, 111.7, 128.0, 129.9, 132.6; IR (neat) 3546 (bm), 1630 (w), 1428 (s), 1111 (vs) cm^{-1}; LRMS 259 (100), 199 (24), 182 (11), 176 (8), 133 (10).

(*R*)-1-(Diphenylpropynylsilyl)prop-2-en-1-ol (26): clear colorless oil (53% yield); R_f = 0.27 (1:4 Et_2O/hexane). Despite several attempts at purification, this material contained approximately 5% unidentified impurities: $[\alpha]_{589}$ = −3.4°; ^1H NMR ($CDCl_3$) δ 1.67 (1 H, bs), 2.07 (3 H, s), 4.62 (1 H, bs), 5.21 (2 H, m), 6.15 (1 H, m), 7.45 (6 H, m), 7.81 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 5.3 (q), 67.5 (d), 77.4 (s), 108.8 (s), 111.7 (t), 128.0 (d), 130.2 (d), 131.9 (s), 132.4 (s), 135.6 (d), 135.7 (d), 138.5 (d); IR (neat) 3450 (bm), 2182 (s), 1631 (w) cm^{-1}; HRMS calcd for $C_{18}H_{18}OSi$ 278.1122, found 278.1130; LRMS 278 (15), 238 (12), 221 (100), 161 (25), 105 (22).

(*R*)-1-(Dimethylphenylsilyl)prop-2-en-1-ol (28): clear colorless liquid (27% yield); R_f = 0.18 (1:9 Et_2O/hexane); ^1H NMR ($CDCl_3$) δ 0.41 (6 H, s), 1.51 (1 H, bs), 4.27 (1 H, bs), 5.16 (2 H, m), 6.04 (1 H, m), 7.44 (3 H, m), 7.63 (2 H, m); ^{13}C NMR ($CDCl_3$) δ −6.1 (q), −5.9 (q), 68.2 (d), 109.9 (t), 127.7 (d), 129.3 (d), 134.1 (d), 136.0 (s), 139.3 (d); IR (neat) 3427 (bm), 1629 (w) cm^{-1}.

(*R*)-1-(Triethylsilyl)prop-2-en-1-ol (30): clear colorless liquid (52% yield); R_f = 0.34 (1:9 Et_2O/hexane); ^1H NMR ($CDCl_3$) δ 0.60 (6 H, q, J = 7.6 Hz), 0.99 (9 H, t, J = 7.6 Hz), 1.53 (1 H, bs), 4.19 (1 H, m), 5.01 (2 H, m), 6.03 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 1.6 (t), 7.2 (q), 67.4 (d), 109.0 (t), 140.4 (d); IR (neat) 3441 (bm), 1629 (w) cm^{-1}; LRMS 205 (8), 172 (12), 157 (22), 143 (13), 115 (77), 103 (58), 87 (100), 75 (52), 59 (45), 55 (20).

(4′-Methylphenyl)(mesitylphenylsilyl)methanol (42): viscous oil; 67% yield (approx 2:1 mixture of diastereomers); ^1H NMR ($CDCl_3$) δ 2.18 (s), 2.20 (s), 2.24 (s), 2.25 (s), 2.30 (s), 5.00–5.20 (2 H, m), 6.82–7.70 (11 H, m); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.2, 24.4, 68.1, 68.3, 125.5, 126.2, 127.9, 128.0, 128.5, 128.8, 129.0, 129.1, 129.5, 133.3, 133.7, 135.3, 135.5, 135.9, 136.2, 139.8, 140.1, 140.7, 145.1, 145.8; IR ($CHCl_3$) 3570, 3040, 2970, 2940, 2170, 1600, 1507 cm^{-1}.

(*R*)-(Diphenylprop-1-ynylsilyl)ethan-1-ol (45): colorless oil (66% yield); ^1H NMR ($CDCl_3$) δ 1.43 (3 H, d, J = 7.0 Hz), 1.52 (1 H, bs), 2.00 (3 H, s), 4.02 (1 H, q, J = 7.0 Hz), 7.35–7.50 (6 H, m), 7.60–7.80 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 5.3, 19.6, 60.1, 77.1, 108.4, 128.0, 130.0, 135.2, 135.4; IR (neat) 3440, 2190, 1425, 1115 cm^{-1}; HRMS calcd for $C_{17}H_{19}OSi$ $(M + H)^+$ 267.1205, found 267.1192.

General Procedure for the Formation of Mosher Esters of the Silylcarbinols. To a chilled (0 °C) solution of (*R*)-(+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetyl chloride[19] (0.31 g, 1.23 mmol) and 4-(dimethylamino)pyridine (0.15 g, 1.23 mmol) in 2 mL of anhydrous CH_2Cl_2 was added silylcarbinol (0.82 mmol). The reaction was allowed to stir at room temperature while being monitored by TLC. When no trace of the starting silylcarbinol could be detected by TLC, the reaction was stirred for at least 1 additional h (to ensure completion and the absence of diastereoselectivity in the formation of the ester). Typical reaction times ranged from 2 h to overnight. The reaction was then cooled to 0 °C and treated with [3-(dimethylamino)propyl]amine (0.24 g, 1.5 mmol). The reaction mixture was then diluted with ether (30 mL) and washed successively with 2 N HCl (3 × 10 mL), saturated $NaHCO_3$ (1 × 10 mL), and brine (1 × 10 mL). After being dried over Na_2SO_4, the ethereal solution was evaporated and the ester analyzed without further purification.

General Procedure for the Acylation of the Silylcarbinols. To a solution of silylcarbinol (4.5 mmol) and 4-(dimethylamino)pyridine (1.1 g, 9.0 mmol) in anhydrous pyridine (10 mL) was added acetic anhydride (0.85 mL, 9.0 mmol) while stirring at room temperature. After the mixture was stirred overnight, the pyridine was removed in vacuo and the residue dissolved in ether (50 mL). The ethereal solution was washed with 1 N HCl (2 × 25 mL), aqueous $NaHCO_3$ (1 × 50 mL), and brine (1 × 50 mL) and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by flash chromatography on silica gel (10% ether/pentane).

(Acetoxy-2′-furanylmethyl)triphenylsilane (31): off-white solid; mp 88–90 °C; 76% yield; ^1H NMR ($CDCl_3$) δ 1.91 (3 H, s), 6.08 (1 H, d, J = 4.1 Hz), 6.21 (1 H, m), 6.58 (1 H, s), 7.38 (16 H, m); ^{13}C NMR ($CDCl_3$) δ 20.5 (q), 61.1 (d), 110.4 (d), 110.6 (d), 127.7 (d), 129.8 (d), 131.9 (s), 135.9 (d), 142.1 (d), 151.7 (s), 170.1 (s); IR ($CDCl_3$) 1728 (s) cm^{-1}; HRMS calcd for $C_{25}H_{22}O_3Si$ 398.1332, found 398.1321; LRMS 398 (2), 276 (13), 261 (8), 260 (24), 259 (100).

[Acetoxy(4′-methoxyphenyl)methyl]triphenylsilane (32): wax; 90% yield; ^1H NMR ($CDCl_3$) δ 2.09 (3 H, s), 3.80 (3 H, s), 6.58 (1 H, s), 6.78 (2 H, B of ABq, J = 8.4 Hz), 7.07 (2 H, A of ABq, J = 8.4 Hz), 7.51 (15 H, m); ^{13}C NMR ($CDCl_3$) δ 20.9 (q), 53.3 (q), 68.9 (d), 113.3 (d), 127.6 (d), 128.9 (d), 129.7 (d), 130.6 (s), 131.8 (s), 136.2 (d), 158.5 (s), 170.2 (s); IR ($CDCl_3$) 1730 (vs) cm^{-1}; HRMS calcd for $C_{28}H_{26}O_3SiLi$ 445.1811, found 445.1813; LRMS 445 (25), 401 (10), 379 (70), 313 (14), 259 (50), 197 (18), 160 (100).

[Acetoxy(4′-methylphenyl)methyl]triphenylsilane ((*R*)-2): wax; 91% yield; R_f = 0.41 in 1:9 Et_2O/hexane; ^1H NMR ($CDCl_3$) δ 2.04 (3 H, s), 2.30 (3 H, s), 6.49 (1 H, s), 6.90 (2 H, B of ABq, J = 8.1 Hz), 6.98 (2 H, A of ABq, J = 8.1 Hz), 7.50–7.28 (15 H, m); ^{13}C NMR ($CDCl_3$) δ 20.7 (q), 69.1 (d), 127.3 (d), 127.5 (d), 127.8 (s), 128.4 (d), 129.7 (d), 131.7 (s), 135.5 (s), 136.1 (d), 169.8 (s); IR (neat) 1739 (s), 1428 (m), 1367 (m), 1228 (vs), 1111 (s) cm^{-1}; HRMS calcd for $C_{28}H_{26}O_2Si$ 422.1695, found 422.1695; LRMS 422 (1), 379 (4), 287 (5), 159 (100), 84 (88), 51 (12).

(1-Acetoxyethyl)triphenylsilane (33): white solid; mp 75–76 °C; 95% yield; ^1H NMR ($CDCl_3$) δ 1.47 (3 H, d, J = 7.4 Hz), 1.99 (3 H, s), 5.62 (1 H, q, J = 7.4 Hz), 7.41 (9 H, m), 7.61 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 17.0 (q), 21.2 (q), 62.5 (d), 128.0 (d), 129.9 (d), 132.4 (s), 136.1 (d), 171.0 (s); IR ($CDCl_3$) 1725 (s), 1430 (m), 1110 (s) cm^{-1}; HRMS calcd for $C_{22}H_{22}O_2SiLi$ 353.1549, found 353.1560; LRMS 259 (100), 241 (35), 199 (12), 181 (28), 105 (23).

(1-Acetoxypropyl)triphenylsilane (34): white solid; mp 85 °C; 97% yield; ^1H NMR ($CDCl_3$) δ 0.94 (3 H, bt, J = 5.6 Hz), 1.87 (2 H, bm), 1.94 (3 H, s), 5.66 (1 H, bt, J = 5.6 Hz), 7.41 (9 H, m), 7.63 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 12.0 (q), 20.9 (t), 25.3 (t), 68.2 (d), 127.9 (d), 129.8 (d), 132.6 (s), 136.1 (d), 171.2 (s); IR (CCl_4) 1739 (m), 1428 (m), 1111 (s) cm^{-1}; HRMS calcd for $C_{23}H_{24}O_2SiLi$ 367.1706, found 367.1705; LRMS 259 (100), 241 (35), 199 (12), 181 (24), 105 (18).

[Acetoxy[3′-(trifluoromethyl)phenyl]methyl]triphenylsilane (35): white solid (84% yield); mp = 108–9 °C; ^1H NMR ($CDCl_3$) δ 2.05 (3 H, s), 6.48 (1 H, s), 7.38 (19 H, m); ^{13}C NMR ($CDCl_3$) δ 20.9 (q), 69.1 (d), 123.5 (d) (C-F, J = 26.0 Hz), 127.9 (d), 128.2, 129.8, 130.0 (d), 130.2, 130.4, 130.9 (s), 136.3 (d), 139.9 (s), 170.3 (s). IR (neat) 1738 (m) cm^{-1}. HRMS calcd for $C_{28}H_{23}F_3O_2Si$ 476.1413, found 476.1414; LRMS 261 (6), 260 (25), 259 (100), 241 (18).

[Acetoxy(3′,4′-difluorophenyl)methyl]triphenylsilane (36): white solid; mp 102–103 °C; 79% yield; ^1H NMR ($CDCl_3$) δ 2.17 (3 H, s), 6.66 (1 H, s), 6.98 (3 H, m), 7.48 (9 H, m), 7.71 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 21.0 (q), 68.6 (d), 116.4 (d) C-F, J = 20.5 Hz), 123.2 (d), 128.0 (d), 130.2 (d), 131.2 (s), 136.0 (s), 136.3 (d), 149.7 (s) (C-F, J = 223.9 Hz), 150.0 (s) (C-F, J = 233.9 Hz), 170.4 (s); IR ($CDCl_3$) 1735 (vs) cm^{-1}; HRMS calcd for $C_{25}H_{19}F_2OSi$ 401.1168, found 401.1200; LRMS 401 (2), 287 (2), 259 (100).

[Acetoxy(3′,5′-difluorophenyl)methyl]triphenylsilane (37): white solid; 55% yield; mp 117.5–119 °C; ^1H NMR ($CDCl_3$) δ 2.04 (3 H, s), 6.39 (1 H, s), 6.48 (2 H, m), 6.55 (1 H, m), 7.43 (15 H,

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m); ^{13}C NMR ($CDCl_3$) δ 20.8 (q), 68.9 (d), 101.8 (d) (C–F (d), J = 26.2 Hz), 109.5 (d) (C–F (t), J = 25.2 Hz), 127.9 (d), 130.2 (d), 130.9 (s), 136.2 (d), 143.1 (s) (C–F, J = 8.8 Hz), 162.5 (s) (C–F (d), J = 235.8 hz), 170.1 (s); IR ($CDCl_3$) 1735 (s) cm^{-1}; HRMS calcd for $C_{27}H_{22}O_2F_2Si$ 444.1351, found 444.1377; LRMS 216 (6), 260 (24), 259 (100), 241 (15).

(1-Acetoxy-2,2-dimethylpropyl)triphenylsilane (38): white solid; 90% yield; mp 92.5 °C; ^1H NMR ($CDCl_3$) δ 1.00 (9 H, s), 1.92 (3 H, s), 5.81 (1 H, s), 7.47 (9 H, m), 7.86 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 20.7 (q), 28.5 (q), 36.3 (s), 75.2 (d), 127.6 (d), 129.4 (d), 133.6 (s), 136.3 (d), 170.4 (s); IR ($CDCl_3$) 1730 (vs) cm^{-1}; HRMS calcd for $C_{24}H_{25}O_2Si$ 373.1617, found 373.1629; LRMS 287 (13), 261 (6), 260 (22), 259 (100), 241 (7), 181 (11), 105 (7), 70 (10), 61 (19).

1-Acetoxy-1-phenyl-1-(phenyldimethylsilyl)methane (39): colorless oil; 86% yield; ^1H NMR ($CDCl_3$) δ 0.36 (3 H, s), 0.40 (3 H, s), 2.13 (3 H, s), 5.94 (1 H, s), 7.10–7.60 (10 H, m); ^{13}C NMR ($CDCl_3$) δ –5.6 (q), –5.4 (q), 21.1 (q), 71.1 (q), 125.5 (d), 126.2 (d), 127.7 (d), 128.1 (d), 129.6 (d), 134.3 (d), 135.1 (s), 139.5 (s), 170.6 (s); IR (neat) 3050, 3025, 2950, 1730, 1360, 1230, 1110, 1020, 830, 790 cm^{-1}.

(4′-Methylphenyl)(mesitylphenylsilyl)methyl acetate (43): viscous oil; 87% yield (approx 1:1 mixture of diastereomers): ^1H NMR ($CDCl_3$) δ 2.27 (3 H, s), 2.39 (6 H, s), 2.48 (6 H, s), 2.54 (3 H, s), 5.56–5.62 (1 H, m), 6.70–7.80 (12 H, m); ^{13}C NMR ($CDCl_3$) δ 20.5 (q), 20.7 (q), 20.8 (q), 24.1 (q), 68.6 (d), 124.9, 126.0, 126.6, 127.7, 128.4, 128.7, 128.8, 129.3, 132.5, 132.8, 134.7, 134.9, 135.9, 136.2, 136.4, 136.5, 139.8, 144.8, 145.3, 170.0 (s); IR (neat) 3030, 2960, 2930, 2250, 2165, 1720, 1600, 1240, 850 cm^{-1}.

1-Acetoxy-1-(diphenylprop-1′-ynylsilyl)ethane (46): colorless oil; 92% yield (mixture of diastereomers); ^1H NMR ($CDCl_3$) δ 2.28 (3 H, s), 2.39 (3 H, s), 2.48 (6 H, s), 2.54 (3 H, s), 5.55–5.65 (m, 1 H), 6.65–6.75 (m, 1 H), 7.0–8.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 5.0 (q), 16.3 (q), 20.9 (q), 62.4 (d), 76.7 (s), 108.3 (s), 127.7 (d), 127.8 (d), 129.9 (d), 131.5 (s), 132.0 (s), 134.9 (d), 135.2 (d), 170.6 (s); IR (neat) 3075, 2975, 2920, 2197, 1725, 1425, 1367, 1260, 1230, 1120, 1035, 700 cm^{-1}.

General Procedure for the Thermolysis of α-Acetoxysilanes. A sample of α-acetoxysilane (0.5 mmol) was placed in a dry ampule (2 mL) and sealed at a pressure of less than 0.1 mmHg. This vessel was then placed in a preheated oven (T = 140–220 °C) for the appropriate amount of time (1–3 h). After being heated, the sample vessel was opened and the contents were analyzed by ^1H NMR spectroscopy. The rearranged silyl acetate was used without further purification since they proved unstable.

(*R*)-Diphenyl(phenyl-*p*-toluoylmethyl)silyl acetate ((*R*)-3): viscous oil; quantitative yield; ^1H NMR ($CDCl_3$) δ 1.97 (3 H, s), 2.34 (3 H, s), 4.85 (1 H, s), 7.00–7.60 (19 H, m).

(±)-Mesitylphenyl-(4′-methylphenyl)methylsilyl acetate (44): colorless oil; quantitative yield; ^1H NMR ($CDCl_3$) δ 1.97 (3 H, s), 2.18 (6 H, s), 2.26 (6 H, s), 2.96 (2 H, s), 6.70–7.00 (6 H, m), 7.30–7.55 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 20.8 (q), 21.0 (q), 22.8 (q), 24.2 (q), 25.0 (t), 126.4 (s), 127.7, 128.6, 128.8, 129.3, 129.8, 133.6, 133.9, 134.1 (d), 135.6 (s), 139.9 (s), 144.8 (s), 170.6 (s); IR ($CHCl_3$) 3030, 2960, 1710, 1600, 1335, 1260 cm^{-1}.

(*S*)-(3′-Pent-2′-ynyl)diphenylsilyl acetate (47): colorless oil; quantitative yield; ^1H NMR ($CDCl_3$) δ 1.23 (3 H, d, J = 7 Hz), 1.73 (3 H, d, J = 3 Hz), 2.16 (3 H, s), 2.87 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 3.6 (q), 10.9 (d), 14.6 (q), 22.6 (q), 77.3 (s), 79.8 (s), 127.7 (d), 130.5 (d), 131.2 (s), 135.4 (d), 170.8 (s).

Dimethyl(diphenylmethyl)silyl acetate (40) and (±)-methylphenyl(1-phenylethyl)silyl acetate (41): colorless oils (quantitative yield of a 70:30 mixture of **40** to **41**, respectively). Dimethyl(diphenylmethyl)silyl acetate (**40**): ^1H NMR ($CDCl_3$) δ 0.36 (6 H, s), 2.03 (3 H, s), 3.98 (1 H, s), 7.20–7.45 (10 H, m). (±)-Methylphenyl(1-phenylethyl)silyl acetate (**41**) as a 1:1 mixture of diastereomers: ^1H NMR ($CDCl_3$) δ 0.60 and 0.65 (3 H, s), 1.41 and 1.50 (3 H, d, J = 6.6 Hz), 2.25 and 2.26 (3 H, s), 2.88 (1 H, q, J = 6.6 Hz), 7.20–7.45 (10 H, m).

General Procedure for the Oxidative Cleavage of the Silafunctional Compounds (Silyl Acetates). A solution of silyl acetate (1.17 mmol) in MeOH/THF (6 mL, 1:1) was sequentially treated with $KHCO_3$ (0.12 g, 1.2 mmol), KF (0.273 g, 4.7 mmol), and H_2O_2 (30%, 1.4 mL, 14.0 mmol). The reaction was warmed to 60 °C for 15 h. The mixture was diluted with ether (100 mL) and washed with saturated $NaHSO_3$ (2 × 100 mL), NaOH (2 N, 2 × 50 mL), NH_4Cl (1 × 50 mL), and brine (1 × 50 mL). After drying over Na_2SO_4, the ether was removed in vacuo and the product was purified by flash chromatography on silica gel (10% ether/pentane).

(*S*)-1-Phenylethanol was obtained in 50% overall yield and 97% ee for the two-step process from **33**.

(*S*)-1-Phenylpropan-1-ol was obtained in 47% overall yield and 98% ee for the two-step process from **34**.

(*R*)-1-Phenyl-1-tolylmethanol was obtained in 51% overall yield and 97% ee for the two-step process from (*R*)-**2**: ^1H NMR ($CDCl_3$) δ 2.39 (3 H, s), 5.83 (1 H, s), 7.10–7.50 (9 H, m).

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Registry No. **1**, 124494-19-5; (*R*)-**2**, 137122-76-0; (*R*)-**3**, 137122-43-1; **5**, 1631-83-0; **6**, 137122-37-3; **7**, 137122-38-4; **8**, 137122-39-5; **9**, 137122-40-8; **10**, 137122-41-9; **11**, 137122-42-0; **13**, 137122-44-2; **14**, 4916-42-1; **15**, 137122-45-3; **16**, 137122-46-4; **17**, 137122-47-5; **18**, 137122-48-6; **19**, 137122-49-7; **20**, 137122-50-0; **21**, 137122-51-1; **22**, 137122-52-2; **23**, 137122-53-3; **24**, 137122-54-4; **25**, 137122-55-5; **26**, 137122-56-6; **27**, 137122-57-7; **28**, 137122-58-8; **29**, 137122-59-9; **30**, 137125-17-8; **31**, 137122-60-2; **32**, 137122-61-3; **33**, 56042-04-7; **34**, 137122-62-4; **35**, 137122-63-5; **36**, 137122-64-6; **37**, 137122-65-7; **38**, 137122-66-8; **39**, 137122-67-9; **40**, 137122-68-0; **41** (isomer 1), 137122-69-1; **41** (isomer 2), 137122-77-1; **42** (isomer 1), 137122-70-4; **42** (isomer 2), 137122-79-3; **43** (isomer 1), 137122-71-5; **43** (isomer 2), 137122-80-6; **44**, 137122-72-6; **45**, 137122-73-7; **46**, 137122-74-8; **47**, 137122-75-9; (+)-Ipc_2BCl, 112246-73-8; (–)-Ipc_2BCl, 85116-37-6; Ph_3SiCl, 76-86-8; *t*-$BuPh_2SiCl$, 58479-61-1; 1-(1′-ethoxyethoxy)-1,2-propane, 20524-89-4; methyl vinyl ether, 107-25-5; propyne, 74-99-7; (*S*)-1-phenylethanol, 1445-91-6; (*S*)-1-phenylpropan-1-ol, 613-87-6; (*R*)-(+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetyl chloride, 137122-78-2.

Supplementary Material Available: Tables of crystal data and structure refinement, atomic coordinates and isotropic thermal parameters for non-hydrogen atoms, bond distances and bond angles, selected torsion angles, anisotropic thermal parameters, and atomic coordinates for hydrogen atoms for **13**; NMR spectra of compounds **1–11** and **13–47** (92 pages). Ordering information is given on any current masthead page.